

Mössbauer spectroscopic and magnetic studies of the gel-grown iron(II) tartrate dihydrate crystals

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Abstract : Compounds of iron tartrate are important because of their applications in medicine. Growth of iron(II) tartrate dihydrate crystals was achieved by controlled diffusion in sodium metasilicate gel. The Mössbauer study was carried out to deduce the isomer shift and the quadrupole splitting. The Vibrating Sample Magnetometer (VSM) was used to study the magnetic behaviour of the crystals at different applied magnetic fields. The crystals exhibited paramagnetic nature

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1. Introduction

The growth of crystals from gel is the simplest technique under ambient conditions and a variety of crystals have been grown [1,2]. Iron tartrate compounds are important due to their medical and pharmaceutical applications. For example, the injections of Na–Cr tartrate, K–Cr tartrate and Na–Fe(III) tartrate increase the susceptibility of transplanted sarcoma to X-rays [3]. Except for the report of Henisch *et al* [2] no major study is carried out on gel grown iron tartrate crystals. Only recently, Joseph *et al* [4] characterized the gel-grown iron tartrate dihydrate crystals using TGA and IR spectroscopic studies along with the elemental and chemical analysis. Moreover, Joseph and Joshi [5] also studied the kinetic parameters for pyrolysis from TG curves. The present work is an attempt to

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characterise the gel-grown iron(II) tartrate dihydrate crystals by using the Mössbauer technique as well as to study their magnetic properties with the help of Vibrating Sample Magnetometer (VSM).

2. Experimental techniques

The apparatus used for the crystal growth were glass test tubes of 2.5 cm diameter and 14 cm in length. For the preparation of the gel, AR grade hydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and AR grade tartaric acid were used. The gel was prepared by mixing tartaric acid with sodium metasilicate solution. After setting the gel, the feed solution of hydrated ferrous sulfate was slowly poured along the wall of the test tube without disturbing the gel surface. The gel density was varied between 1.02 to 1.08 gm/cm^3 . The concentration of the tartaric acid was 1 M and that of the hydrated ferrous sulfate solutions were 0.5 M, 1 M and 2 M. Ferrous sulfate solution diffused through the gel and spherulitic crystals of iron(II) tartrate dihydrate ($\text{FeC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$) were grown in the gel. The good quality crystals were grown in the pH range of 3.8 to 4.2 with specific gravity of 1.06 to 1.075 at room temperatures. Three different types of growth were observed; (1) large number of very small black clusters of 2–3 mm diameter were found at the liquid-gel interface and below that upto 1 cm thick region of white spongy colloidal precipitates, (2) black coloured spiky spherulitic crystals of 4 to 5 mm diameter were observed 1.5 cm below the liquid gel interface inside the gel, and (3) spherulitic crystals with light greenish colour having diameter of 1 to 3 mm were grown at the bottom of the test tubes. These results correspond to the observations of Raina [6] on the rare-earth tartrates which are reported elaborately elsewhere [4].

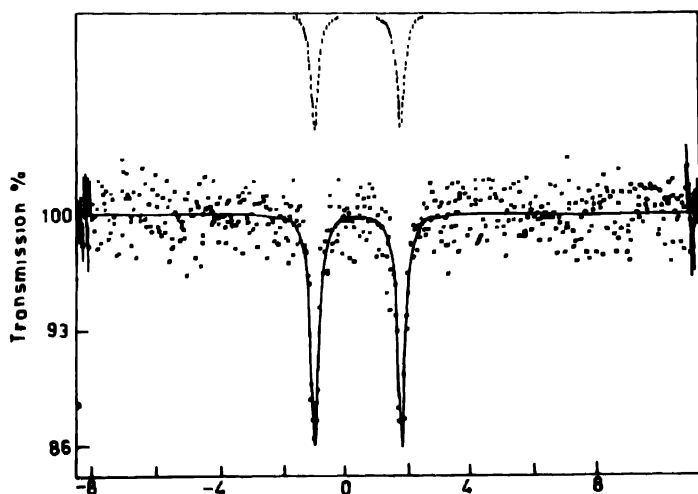


Figure 1. Mössbauer spectrum of the samples grown at gel-liquid interface.

The Mössbauer spectra were recorded in the transmission geometry with a constant acceleration transducer and a 512 channel multichannel analyser. A ^{57}Co (Rh) source of activity 10 m Ci was used. The solid lines through the data points are the results of computer fit of the data. Figures 1–3 show the Mössbauer spectra for all the three types of crystals. The magnetic susceptibility for all the three types of crystals was measured using

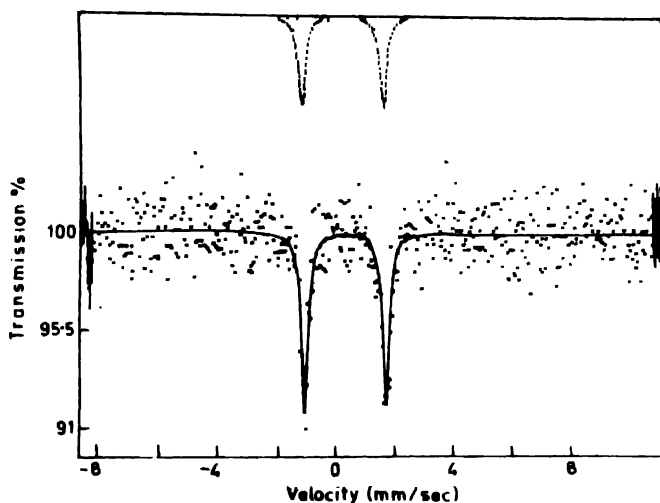


Figure 2. Mössbauer spectrum of the samples obtained below the gel-liquid interface

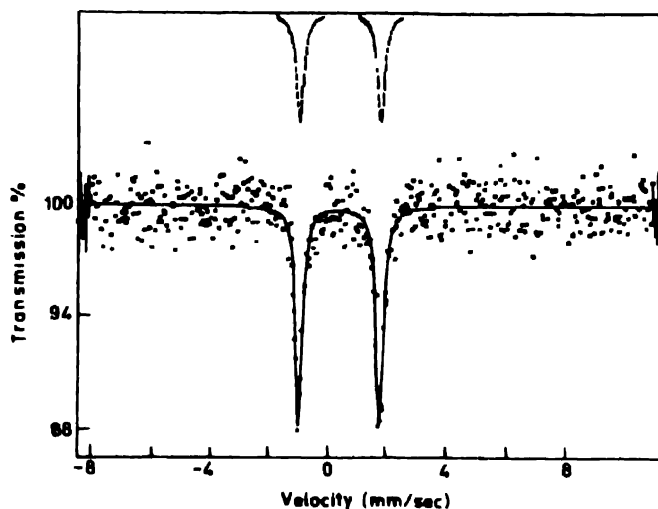


Figure 3. Mössbauer spectrum of the samples grown at the bottom of the test tubes.

EG and G PARC-155 Vibrating Sample Magnetometer at room temperature with different applied magnetic fields. Also the elemental analysis was carried out with the help of atomic absorption spectroscopy (AAS). The atomic absorption spectroscopic analysis was done on

2380 Perkin-Elmer spectrometer using Fe lamp for iron elemental analysis. The samples were dissolved in a suitable solvent in appropriate dilution as per the standard preparation technique for the analysis [7].

3. Results and discussions

The Mössbauer spectroscopic technique is widely used in a variety of chemical and solid state problems [8–10]. The Coulombic interaction alter the energy separation between the ground state and the excited state of the nucleus, thereby causing a slight shift in the position of the observed resonance line, which is different in various compounds and hence called as the chemical isomer shift. Another parameter through which information on the nature of the chemical bond can be obtained, is the electric quadrupole interaction between the quadrupole moment of the nucleus and the electric field gradient at the nucleus due to the asymmetric distribution of charges either on the ion itself and/or in the crystal. These two parameters of major interest have been studied in various organic and inorganic iron compounds. Ferrous fluoride was investigated by Mössbauer spectroscopy [11], which have a large quadrupole splitting in the paramagnetic state [12]. De Benedetti *et al* [13] studied the Mössbauer spectrum of Fe^{2+} ion in an absorber of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at liquid nitrogen temperature and calculated the chemical shift and the electric quadrupole splitting. Apart from this, Mössbauer spectroscopic studies on several iron compounds were carried out by several investigators. The Mössbauer isomer shift of ferrous phenanthroline and related compounds was reported by Epstein [14]. The Fe(III) formate, acetate, monochloroacetate, trichloroacetate, phenylacetate and bezoate complexes exhibited quadrupole line asymmetry in the Mössbauer spectra [15]. Epstein *et al* [16] reported a Mössbauer study of frozen $\text{Fe}(\text{NO}_3)_3$ -citric acid-NaOH solutions, which indicated that the isomer shift is not a strong function of pH but there was a trend towards larger quadrupole splitting at higher pH values, whereas the Mössbauer study of anhydrous ferrous formate was carried out by Pipman and Ron [17]. However, recently the Mössbauer spectroscopic study of some iron(II) dicarboxylates has been carried out by Vikumbh *et al* [18], as well as the Mössbauer studies on natural chromites by Das *et al* [19].

Takashima and Ohashi [20] investigated various inorganic compounds and later on Takashima and Tateishi [21] extended their investigation to variety of organic iron chelates using the Mössbauer technique. It was suggested that the magnitude of the isomer shift could be related to the details of the bonding between iron and the ligands. Takashima and Takeishi [21] obtained the values of the isomer shift (δ) and the quadrupole splitting (ϵ) for iron(III) tartrate as +0.44 mm/sec and 0.25 mm/sec, respectively, as well as for iron(II) tartrate monohydrate as +1.47 mm/sec and 1.31 mm/sec, respectively. Probably this was the only major work reported in literature on the Mössbauer studies of iron-tartrate compounds so far. It was noted [13] that there was negligible quadrupole splitting in the case of ionic ferric compound because of its $3d^5$ electron configuration. However, most of the organic

chelates exhibited splitting, which was caused by the field gradient from the neighbouring atoms rather than by the iron atoms itself [21]. The magnitude of the quadrupole splitting can be a measure of the crystallographic symmetry.

The Mössbauer spectra at room temperature for the three types of crystal samples are displayed in Figures 1–3 and the parameters deduced are listed in Table 1. All the samples gave a large quadrupole splitting in the paramagnetic state indicating that the iron ions have

Table 1. The values of chemical isomer shift and quadrupole splitting for all the three types of crystals.

Type of sample	Isomer shift* mm/sec (± 0.04)	Quadrupole splitting mm/sec (± 0.04)
Sample-I, At gel-liquid interface	1.22	2.78
Sample-II, Below the gel-liquid interface	1.20	2.79
Sample-III, At the Bottom of the test tube	1.23	2.77

* with respect to Fe metal.

a non-cubic environment. It is also seen that the chemical isomer shift and the quadrupole splitting remain uninfluenced by the crystal growth history of the samples. The present values of quadrupole splitting and chemical isomer shift are different from the earlier reported values of iron(II) tartrate monohydrate [21], which is due to the different chemical environment produced by chemically attached two molecules of water of hydration in the crystal. The atomic absorption spectroscopy data for all the three samples are given in Table 2, which indicate that the crystals become more and more enriched with iron on

Table 2. The atomic absorption spectroscopic data for elemental analysis of the samples

Type of sample	Content of Fe
Sample-I At gel-liquid interface	705 ppm
Sample-II Below gel-liquid interface	1250 ppm
Sample-III At the bottom of the test tube	1335 ppm

going towards the bottom of the test tubes. Also from elemental analysis, it has been observed that the percentage of carbon and hydrogen is highest in the crystals grown at the bottom of the test tube, which is tabulated along with the theoretical percentage values of

carbon and hydrogen in the crystals by Joseph *et al* [4]. This further, suggests that the crystals grown at the bottom of the test tubes were more perfect and pure in conformity with the IR spectroscopy results [4].

The Vibrating Sample Magnetometer (VSM) was developed by Foner [22] which is based on the flux change in a coil when sample is vibrated near it. This method is found to be very versatile and sensitive and has been modified further by several workers [23,24]. Table 3 shows the values of magnetic moments for all the three samples at different values

Table 3. The vibrating sample magnetometer (VSM) data at room temperature for all the three types of crystals

Type of sample	Applied magnetic field. (Tesla)	Magnetic moment (EMU)	Bulk susceptibility ($A\ m^2/kg\ T$)
Sample-I, At gel-liquid interface	0.2	$+ 0.198 \times 10^{-2}$	8.319×10^{-6}
	0.4	$+ 0.364 \times 10^{-2}$	7.647×10^{-6}
	0.6	$+ 0.638 \times 10^{-2}$	8.935×10^{-6}
	0.8	$+ 0.832 \times 10^{-2}$	8.739×10^{-6}
	1.0	$+ 0.875 \times 10^{-2}$	7.352×10^{-6}
Sample-II, Below gel-liquid interface	0.2	$+ 0.249 \times 10^{-2}$	7.410×10^{-6}
	0.4	$+ 0.446 \times 10^{-2}$	6.637×10^{-6}
	0.6	$+ 0.605 \times 10^{-2}$	6.002×10^{-6}
	0.8	$+ 0.752 \times 10^{-2}$	5.595×10^{-6}
	1.0	$+ 0.940 \times 10^{-2}$	5.595×10^{-6}
Sample-III, At the bottom of the test tube	0.2	$+ 0.347 \times 10^{-2}$	6.024×10^{-6}
	0.4	$+ 0.648 \times 10^{-2}$	5.625×10^{-6}
	0.6	$+ 0.928 \times 10^{-2}$	5.370×10^{-6}
	0.8	$+ 1.230 \times 10^{-2}$	5.339×10^{-6}
	1.0	$+ 1.470 \times 10^{-2}$	5.104×10^{-6}

of magnetic field at room temperatures. It can be easily seen that the magnetic moment increases with the applied magnetic field, but the bulk susceptibility remains more or less constant. Altogether these are found to be largest for the crystals grown at the gel-liquid interface. This suggests the paramagnetic behaviour of the crystals.

4. Conclusions

The crystals grown at the bottom of the test tubes containing sodium metasilicate gel are more refined and enriched with iron than the crystals grown at the gel-liquid interface. The difference in values of the chemical isomer shift and the quadrupole splitting from earlier reported values is due to the different chemical environment and more number of molecules of water of hydration attached with iron tartrate. The VSM data suggest the paramagnetic nature of the crystals and the values of magnetic susceptibilities are largest for crystals grown at the gel-liquid interface.

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